Polymorph Selectivity under Nanoscopic Confinement: Crystallization in Nanoreactor (IRG-1).
Graduates students Jeong-Myeong Ha and Joanna Wolf, working with Ward and Hillmyer, demonstrated that polymorph selectivity can be achieved during crystallization of anthranilic acid (AA) and 5-methyl-2-[(2-nitrophyenyl)amino]-3-thiophenecarbonitrile (ROY) within nanoporous glass beads and polymer monoliths. Both of these organic materials are considered benchmarks of polymorphic behavior, and ROY also is an important pharmaceutical intermediate in the manufacturing of the commercial drug olanzapine. Whereas polymorph III of
AA crystallizes from the melt on nonporous glass beads or within larger pores, the metastable polymorph II crystallizes in pores with diameters <23 nm, with the selectivity toward this form increasing with decreasing pore size. Of the six ROY polymorphs characterized by single-crystal
X-ray diffraction, only the red form (R) crystallizes in the pores. These observations suggest that nucleation and polymorph selectivity is governed by critical size constraints imposed by the
ultrasmall pores, thereby providing fundamental insights into the nucleation process itself. The ability to achieve polymorph selectivity in both glass and polymer matrices suggests wide-ranging compatibility with various organic crystalline solids, promising a new approach to controlling polymorphism and searching for unknown polymorphs. This is a crucial materials science issue in the pharmaceutical and specialty chemicals industries, where crystal structure as well as composition often influences performance. For example, the purity and bioavailability of a pharmaceutical depends on the crystal structure of the polymorphic form (currently, the Food and Drug Administration approves a product and its intermediates based on their polymorphs as well as their compositions). [Ha, J.-M.; Wolf, J.H.; Hillmyer, M.A.; Ward, M.D. Regulating
Polymorph Selectivity Through Confined Crystallization in Nanopores. J. Am. Chem. Soc.
ASAP (Web)]

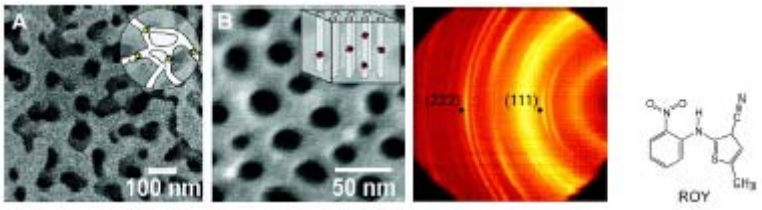

Figure. Scanning electron micrographs of (A) commercially available controlled porous glass (CPG) with a pore diameter (d=55 nm) and (B) a platinum-coated (ca.. 2 nm thick) porous PCHE monolith with a hexagonal array of cylindrical pores (d=30 nm). (Insets) Schematic representations of nanocrystals grown in the pores. The rightmost panel is the diffraction pattern of nanocrystals of the R form of ROY grown in the PCHE monolith pores.

Silicon Nanoparticles (Seed). In a joint IGERT-MRSEC effort, graduate students Ameya Bapat and Christopher Perrey, with Campbell, Kortshagen, and collaborator Barry Carter, developed two processes for making nanocubes: cubic single crystal silicon nanoparticles. These particles have (100) faces and are typically about 40 nm in diameter. Due to the flat, crystalline surface, they are highly aligned with the substrate surface normal. High concentrations of these particles can be made in a silane/argon plasma by operating the plasma at sufficiently high pressure so that one gets filamentary arcs between the electrodes. These arcs appear to last for milliseconds. The plasma density in these arcs is sufficiently large that the particles emitted have the characteristic cubic shape. The fact that these particles are created in the aerosol means that we are able to deposit single crystal silicon on any type of substrate, even on soft materials such as plastics, promising a unique approach to the fabrication of ultrasmall silicon-based transistors. [Bapat, A.; Perrey, C.R.; Campbell, S.A.; Carter, C.B.; Kortshagen, U. Synthesis of Highly Oriented, Single-crystal Silicon Nanoparticles in a Low-pressure Inductively Coupled Plasma. J. Appl. Phys. 2003, 94, 1969].

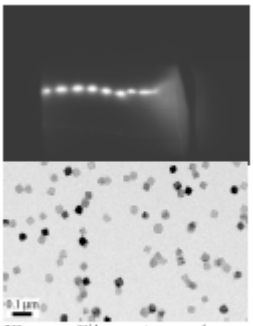

Figure. Filamentary plasma (top) and Si nanocubes (bottom).

Structural Characterization of an OTFT Pentacene Monolayer (IRG 2). Graduate students Sandy Fritz and Stephen Martin, with Ward, Frisbie, and new collaborator Michael Toney (Stanford Synchrotron Radiation Laboratory, SSRL) used synchrotron grazing incidence X-ray diffraction to demonstrate that a pentacene monolayer, grown on an amorphous SiO2 substrate that is commonly used as a dielectric layer in organic thin film transistors (OTFTs), is crystalline. A preliminary energy-minimized model of the monolayer, based on the GIXD data, revealed that the pentacene molecules adopt a herringbone arrangement with their long axes tilted slightly from the substrate normal. Although this arrangement resembles the general packing features of the (001) layer in single crystals of bulk pentacene, the monolayer lattice parameters and crystal structure differ from those of the bulk. Because carrier transport in pentacene OTFTs is presumed to occur in the semiconductor layers near the dielectric interface, the discovery of a crystalline monolayer structure on amorphous SiO2 has important implications for transport in OTFTs. [Fritz, S.; Martin, S.M.; Frisbie, C.D.; Ward, M.D.; Toney, M.F. Structural Characterization of a Pentacene Monolayer on Amorphous SiO2 with Grazing Incidence X-ray Diffraction. J. Am. Chem. Soc. ASAP (Web).]

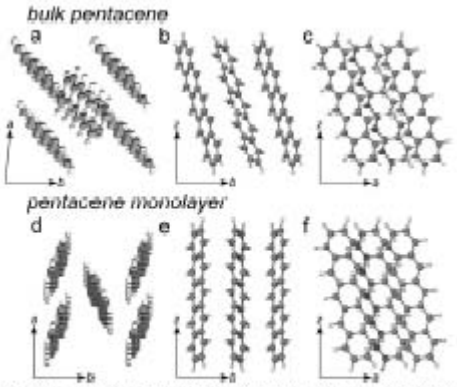

Figure. Normal views of the ab planes of bulk pentacene and the model monolayer structures (left) and the respective side views (center, right). The z-axis is the normal to the ab plane.